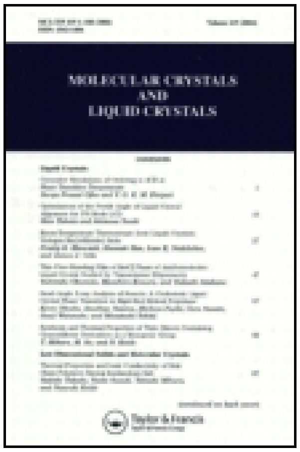

Molecular Crystals and Liquid Crystals

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Molecular Alignment in Nematic Liquid Crystals

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Molecular Alignment in Nematic Liquid Crystals

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The relative effectiveness of electric and magnetic fields on the molecular alignment in the nematic phase, of *p*-methoxy and *p*-ethoxy *p'*-*n*-butyl azo benzenes exhibiting positive dielectric and positive conductivity anisotropies, using rf dielectric constant measurements at 1 MHz and different moderately thick samples are carried out. It is found that, in low frequencies conductivity anisotropy plays a dominant role and in high frequencies relative effectiveness of electric and magnetic fields on the molecular alignment is independent of thickness of the sample in 100–500 μm range. The optical observations are correlated to the changes in molecular alignment and dielectric constant measurements. The behaviour of the distortion of twist in a twisted nematic liquid crystal in the presence of electric fields is also investigated using rf dielectric constant measurements.

INTRODUCTION

Measurement of dielectric constant, ϵ, at 1 MHz in presence of low frequency external electric field and magnetic fields to infer regarding the molecular alignment in negative dielectric and positive conductivity anisotropic liquid crystals MBBA and EBBA has been already reported.[1,2] The results are in fair agreement with the results of Carr and his coworkers[3-7] on molecular alignment employing microwave techniques. It was clear from Carr *et al.*'s work that the conduction induced anomalous alignment in low frequency electric fields can be observed in all commercial samples of liquid crystals unless purification was done by special methods such as chromatographic purification, zone refining, vacuum distillation followed by recrystallisation etc.

The liquid crystals can be classified into four categories. (1) [$-$, $+$][3]; (2) [$-$, $-$][4]; (3) [$+$, $+$][5] and (4) [$+$, $-$][6]. The first and second signs in the parenthesis correspond to dielectric and conductivity anisotropies respectively.

The molecular alignment of liquid crystals possessing positive dielectric anisotropy is parallel with the electric field. The molecular alignment of liquid crystals with negative dielectric anisotropy is perpendicular with the electric field. Anomalous alignment of liquid crystals in electric fields refers to the phenomenon of molecular alignment other than that predicted from consideration of dielectric anisotropy alone. In all the cases where anomalous alignment was observed the direction of the maximum conductivity is parallel to the electric field. The anomalous alignment occurs only in low frequency region where accumulated charges, resulting from the conductivity anisotropy, follow the field reversals. In high frequency electric fields the charges cannot follow the field reversals. Thus the molecular alignment in high frequency electric fields is purely dependent upon dielectric anisotropy. The molecular alignment studies in all possible combinations of dielectric and conductivity anisotropies were reported by Carr and his coworkers. The results are briefly described in Table I.

The important observations regarding domains and dynamic scattering in positive dielectric anisotropic liquid crystals are reviewed briefly. Elliot and Gibson[9] observed domains and light scattering in *p*-anisal *p*′-amino azo benzene. Heilmeier *et al.*[10] correlated the occurrence of dynamic scattering in liquid crystals to the dipole moment of the molecules. Liquid crystal molecules (*p*-anisal amino phenyl *p*-acetate) having the dipole moment perpendicular to the long axis exhibit dynamic scattering, while molecules (*p*-ethoxy benzylidene *p*′-cyano aniline) having the dipole moment parallel to the long axis exhibit no or little dynamic scattering. Gruler and Meier[11] reported that the occurrence of dynamic scattering in liquid crystals is dependent on the dielectric anisotropy rather than on the dipole moment. The liquid crystals having positive dielectric anisotropy exhibit no dynamic scattering while liquid crystals with negative dielectric anisotropy exhibit dynamic scattering. This can also explain the observations of Heilmeier *et al.* Gruler and Meier,[12] however, correlated the domains formation to the initial molecular alignment with respect to the electric field, imposed either by magnetic field or other methods. In both positive and negative dielectric anisotropic liquid crystals, when the molecules are initially aligned perpendicular to the electric

TABLE I

Molecular alignment of nematic liquid crystals in presence of electric fields

Name of the compound	Nature of anisotropies		Molecular alignment with respect to electric field	Reference
	dielectric	conductivity		
N(*p*-methoxybenzylidene) *p*-*n*-butylaniline (MBBA)	– ve	+ ve	Parallel in low frequencies and perpendicular in high frequencies	Parker and Carr
p,*p*′-di-*n*-Heptyloxy azoxybenzene (HOAB)	– ve	– ve	Low frequency electric fields are more effective than high frequency electric fields in causing perpendicular alignment	Mclemore and Carr
p-*n*-Butyloxybenzoic acid (BOBA)	+ ve	+ ve	Low frequency electric fields are more effective than high frequency electric fields in causing parallel alignment	Flint and Carr
p-*n*-Nonyloxybenzoic acid (NOBA)	+ ve	– ve	Perpendicular in low frequency and parallel in high frequencies	Chou and Carr

field, domains appear at a threshold voltage. When the molecules are initially aligned parallel to the electric field no domains appeared in positive dielectric anisotropic liquid crystals, while domains appeared at a threshold voltage only in one direction in the negative dielectric anisotropic liquid crystals. Their investigations include the sample *p*-methoxy *p'*-*n*-butyl azo benzene, MBAB, which is used in the present work. In pure MBAB when molecules are aligned parallel to the electric field no domains appeared. In a mixture exhibiting positive dielectric anisotropy containing MBAB as one of the components, domains appeared when the molecules are initially aligned perpendicular to the electric field. deJeu *et al.*[13-15] observed domains, loop domains and reorientation in samples with different grades of purity and emphasized that the instabilities in positive dielectric anisotropic liquid crystals are not purely dielectric in origin but are associated with hydrodynamic flow just as for nematics with negative dielectric anisotropy. Their work inferred that the type of instability is determined by the direction of the dielectric torque. They concluded that the orientating torques on the nematic mesophase by the electric and magnetic fields determine whether a hydrodynamic instability becomes visible as a domain pattern or as reorientation.

Flint and Carr[6] observed dynamic scattering in a positive dielectric anisotropic liquid crystal, *p*-*n*-butyloxy benzoic acid which is an exception. They suggested that dynamic scattering resulted from ionic conductivity present in the sample. However, their work do not indicate why the dSM does not occur in other positive dielectric anisotropic liquid crystals having conductivity effects. Carr, Flint and Parker correlated the domain formation to the interaction of torques due to dielectric and conductivity anisotropies i.e.,

torque due to $\Delta\sigma >$ torque due to $\Delta\epsilon$: domains appear
torque due to $\Delta\sigma <$ torque due to $\Delta\epsilon$: domains will not appear
torque due to $\Delta\sigma =$ torque due to $\Delta\epsilon$: domains appearance is questionable

The present work describes the molecular alignment studies using the dielectric constant measurements at 1 MHz and the relative effectiveness of electric and magnetic fields on the moderately thick samples and its dependence on the thickness of the samples. The samples are *p*-methoxy *p'*-*n*-butyl azo benzene, MBAB and *p*-ethoxy *p'*-*n*-butyl azo benzene EBAB. Both the compounds exhibit positive dielectric and positive conductivity anisotropies i.e., [+, +] systems.

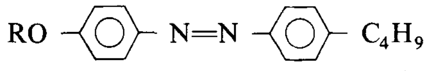
TABLE II

Dielectric constants and conductivity ratios of MBAB and EBAB

Sample	Temperature	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	$\Delta\epsilon$	$\sigma_{\parallel}/\sigma_{\perp}$
MBAB	32 °C	3.60	3.40	+0.20	1.5
EBAB	53 °C	3.08	2.85	+0.23	1.2

EXPERIMENTAL

The MBAB and EBAB were synthesized following the standard procedure. The crude products were purified by column chromatography (silica gel finer than 200 mesh and benzene as eluent). The eluted compound was recrystallised twice from hexane. The transition temperatures and molecular formulae are presented below.



$$R = CH_3 : \text{MBAB Solid} \overset{31\,^\circ C}{\longleftrightarrow} \text{Nematic} \overset{48\,^\circ C}{\longleftrightarrow} \text{Isotropic}$$

$$R = C_2H_5 : \text{EBAB Solid} \overset{48\,^\circ C}{\longleftrightarrow} \text{Nematic} \overset{85\,^\circ C}{\longleftrightarrow} \text{Isotropic}$$

The investigations on the molecular alignment were carried out using the dielectric constant measurements at 1 MHz. Optical observations were made through a long focal length travelling microscope. Both the compounds exhibit positive dielectric and positive conductivity anisotropies i.e., [+, +] systems. The values of the dielectric constant parallel and perpendicular to the long axes of the molecules and the conductivity ratio are presented in Table II.

RESULTS AND DISCUSSION

A. Frequency dependence of molecular alignment

In presence of an electric field, the long molecular axes of the nematic liquid crystals with positive dielectric anisotropy will align with the electric field, while with magnetic field also they align because of its positive diamagnetic anisotropy. In presence of crossed electric and magnetic fields, the increase in electric field intensity causes a change in molecular orientation from the perpendicular alignment imposed by magnetic field to be parallel with the electric field. Figure 1 shows the variation of molecular alignment in MBAB, in terms of ϵ with the electric field at different frequencies when magnetic field was applied perpendicular to the electric field. $\epsilon = \epsilon_{\perp} = 3.40$ corresponds to the molecular alignment parallel to the magnetic field and perpendicular to the electric field, while $\epsilon = \epsilon_{\parallel} = 3.60$ corresponds to the molecular alignment parallel to the rf electric field and magnetic field.

The variation in ϵ from $\epsilon_{\perp} = 3.40$ to $\epsilon_{\parallel} = 3.60$ gives the information regarding the changes in molecular alignment. At different frequencies, as the strength of the electric field is increased the long axes of the molecules rotate 90° in approaching a parallel alignment with the electric field. The threshold electric field for causing a change in the molecular alignment, increases with the frequency up to 150 Hz. At

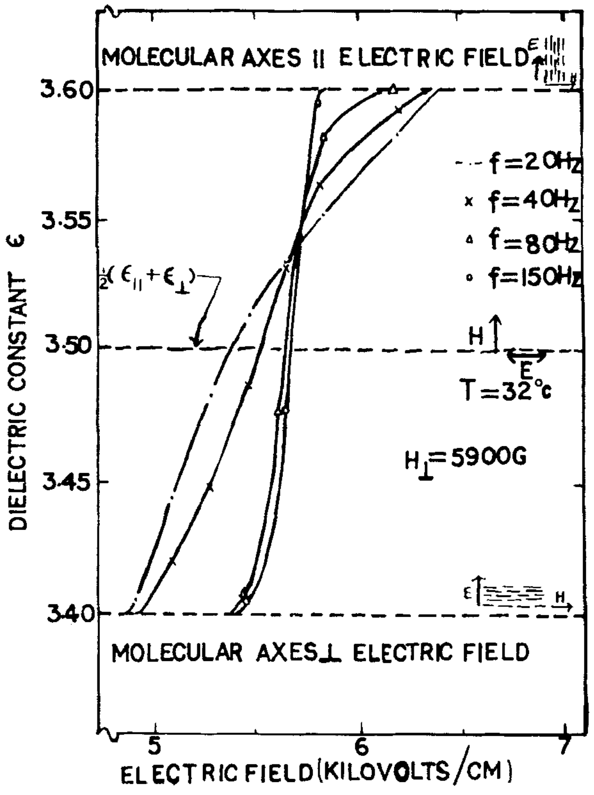


FIGURE 1 Dielectric constant ϵ of MBAB at 1 MHz as a function of externally applied electric fields of various frequencies. A static magnetic field of 5900 G was applied perpendicular to the external field which was parallel to rf field $T = 32°C$.

and above 150 Hz the plots of ϵ vs E. F. at different frequencies superimpose on one other, i.e., the threshold electric field to cause a change in molecular alignment from perpendicular direction is constant at different frequencies. The range of field strengths required to cause a change in molecular reorientation through 90°, is larger in low frequencies than in the high frequencies. As the frequency is increased the width of the electric field strength, to cause such a reorientation through 90°, decreases. At and above 150 Hz i.e., in high frequency region sudden switching over of the molecules occurs.

In low frequencies the torques due to conductivity and dielectric anisotropies aid each other in causing a parallel molecular alignment with the electric field. In high frequencies the torque due to conductivity anisotropy vanishes, thereby enabling the torque due to dielectric anisotropy to cause the molecular alignment. The involvement of conductivity anisotropy in molecular alignment, and large range of field strengths in low frequencies, is anomalous and is similar to the mechanism responsible for anomalous alignment in negative dielectric anisotropy liquid crystals. In high frequencies the dielectric anisotropy is the responsible process for molecular alignment which is indicated by sudden switching over of the molecules.

If the electric and magnetic fields are applied such that the preferred direction of nematic director $\vec{n}$ due to the electric field is normal to that preferred by the magnetic field and the director makes an angle of 45° with each of the fields, then the following empirical relations 1 and 2 suggested by Carr are satisfied

$$(E/H)^2 = 9 \times 10^4(\mu_{\parallel} - \mu_{\perp})/(\epsilon_{\parallel} - \epsilon_{\perp}) \tag{1}$$

$$(E/H)^2 = 9 \times 10^4(\mu_{\parallel} - \mu_{\perp})/[(\epsilon_{\parallel} - \epsilon_{\perp}) + C] \tag{2}$$

From equation 2 the effective electric field for a random orientation of molecular alignment must increase with the decrease in C. The results shown in Figure 1 indicate that the low frequency electric fields are more effective in changing the orientation of the long axes of the molecules. It is also evident from Figure 1 that the effective electric field for random orientation increases with the frequency. Since 'C' a term associated with conductivity anisotropy vanishes above the cut off frequency, the E/H value must be constant for random orientation of molecules at different frequencies above cut-off frequency. The results of ϵ vs E above cut off frequency = 150 Hz, are same at different frequencies. The results are qualitatively same for EBAB at 53°C except the cut off frequency is 300 Hz. This sudden switching over of molecules through 90° involves purely dielectric effect which is analogous to Fredericks Z transition.

B. Molecular alignment in high frequency electric field

To check the validity of the equation 1 the relative effectiveness of electric and magnetic fields in producing molecular alignment is investigated in 150 Hz electric field strengths and for different thickness of samples of MBAB. Figure 2 shows the variation of ϵ with the externally applied electric field parallel to the rf measuring field and perpendicular to the magnetic field, (the thickness of the sample = 275

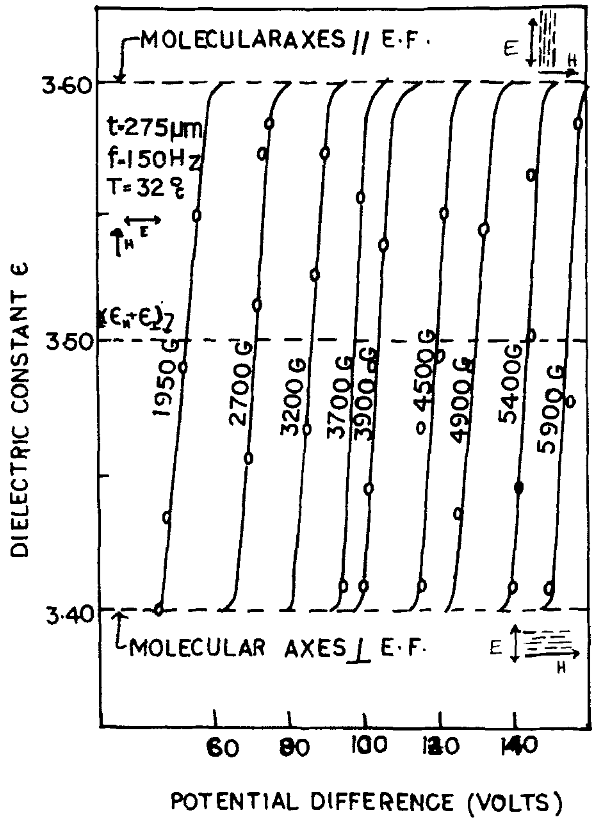


FIGURE 2 Dielectric constant ϵ of MBAB at 1 MHz as a function of an externally applied potential difference. The individual curves are for various values of a static magnetic field applied perpendicular to the external electric field which was parallel to rf field. $T = 32\,^\circ C$, thickness = 275 μm.

TABLE IIIa

Ratios of electric field to magnetic field corresponding to a random orientation of the molecules employing 150 Hz electric field in MBAB for different thick samples

$H \perp E\ f = 150$ Hz					
Thickness = 170 μm		Thickness = 225 μm		Thickness = 275 μm	
H gauss	E/H Volts/cm. gauss	H gauss	E/H Volts/cm. gauss	H gauss	E/H Volts/cm. gauss
3350	0.97	3400	0.97	2700	0.96
3600	0.97	4000	0.98	3350	0.96
4200	0.97	4500	0.96	3700	0.97
4750	0.97	5100	0.96	3900	0.97
5500	0.97	5500	0.97	4500	0.97
6000	0.97	6000	0.97	5400	0.96
				5900	0.96

TABLE IIIb

Ratios of electric field to magnetic field corresponding to a random orientation of the molecules employing 500 Hz electric field in EBAB for 275 μm thick sample

$H \perp E\ f = 500$ Hz	
H gauss	E/H Volts/cm. gauss
2500	0.93
3000	0.94
3500	0.94
4000	0.94

μm). In equation 1 $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\mu_{\parallel}$ and $\mu_{\perp}$ are constants, where conductivity forces cease to operate, during the course of the experiment and thus one can check the validity of the equation by varying E and H.

The calculated values of E/H for different thickness of samples at different magnetic field strengths are presented in Table IIIa. The value of $(E/H) = 0.97$ volts/cm. gauss is fairly constant and is independent of sample thickness, which shows that wall effects are almost negligible in these moderately thick samples. The E/H value for EBAB, at 53°C, $f = 500$ Hz, is 0.94 volts/cm. gauss (Table IIIb).

C. Average state of alignment

Measurements of the high frequency dielectric constant are used to provide some information about the average state of alignment and the results shown in Figures 1 and 2 can be described as follows.

When the nematic director i.e., molecular axes is perpendicular to electric field, for $\epsilon = \epsilon_\perp = 3.40$, the state of alignment corresponds to the parallel alignment of molecules with the magnetic field and an electric field perpendicular to the magnetic field but below threshold values. The dotted line $(\epsilon_\parallel + \epsilon_\perp)/2$ represents an ordering such that the average angle of rotation for the directors is 45° with respect to the initial alignment i.e., the average nematic order parameter of the sample is 45° to both the electric and magnetic fields. (Figures 1 and 2.)

D. Optical observations

Broken domains appear both in MBAB and EBAB in the low frequency electric field which are unlike the stable domains in MBBA. The threshold voltage necessary at which the broken domains are first observed is the same voltage at which the change in molecular orientation occurs and is indicated by the change in dielectric constant from $\epsilon = \epsilon_\perp = 3.40$ in Figure 1, for every frequency in low frequency regime. This phenomena can be explained as that the molecules are initially aligned perpendicular to the electric field and the appearance of broken domains coincide with the onset of change in molecular alignment from the perpendicular direction to parallel orientation. As the strength of the electric field is increased the broken domains change into nucleated weak turbulence in certain regions and finally the molecules reorient with the electric field. The observed weak turbulence is not alike the intense turbulence viz., dynamic scattering mode in MBBA or EBBA. The reorientation is indicated by the increase in the transparency of the liquid crystal film. At high frequencies near the dielectric regime only loop domains followed by reorientation are observed as a transient effect in the increasing order of the electric field. The nucleated weak turbulence is not seen in high frequency electric fields, $f \geq 150$ Hz. The loop domains are regions where the nematic director is still parallel to the walls in surroundings that have started to align with the electric field. In the dielectric regime only loops and reorientation are observed. The change in dielectric constant $\epsilon = \epsilon_\perp = 3.40$ in high frequency region i.e., $f \geq 150$ Hz and observation of loop domains or loops occur at the same threshold voltage. When the electric field is switched off instantaneously threads appeared. In MBAB and EBAB where torques due to conductivity anisotropy ≤ torques due to dielectric anisotropy only unstable domains in low frequencies and absence of domains in dielectric regime are observed. These observations are in good agreement with the results of Carr *et al.* and Gruler and Meier.

E. Distortion of twisted MBAB in electric field

For a thin layer of MBAB sandwiched between two previously rubbed plates arranged in crossed configuration, Figure 3 gives the relative changes in the dielectric constant as a function of the electric field applied perpendicular to the electrode surfaces and hence parallel to the helix axis of the twisted MBAB. The critical electric field to cause a distortion of twisted nematic structure is of the order of 5 ~ 6 volts for 170 μm thickness sample. The critical electric field decreases with the increase in frequency i.e., 6 volts for 50 Hz and 5 volts for 150 Hz. At higher electric fields the molecules are aligned with the electric field which is indicated by $\epsilon = \epsilon_{\parallel} = 3.60$ and parallel molecular alignment was found to be independent of frequency but dependent upon the electric field. Thus this method of measuring molecular alignment changes in terms of ϵ in the presence of electric fields can also be used to determine the critical electric field to cause the distortion of twisted nematic structure. Similar results are reported using electric fields through transmitted light intensities.[17]

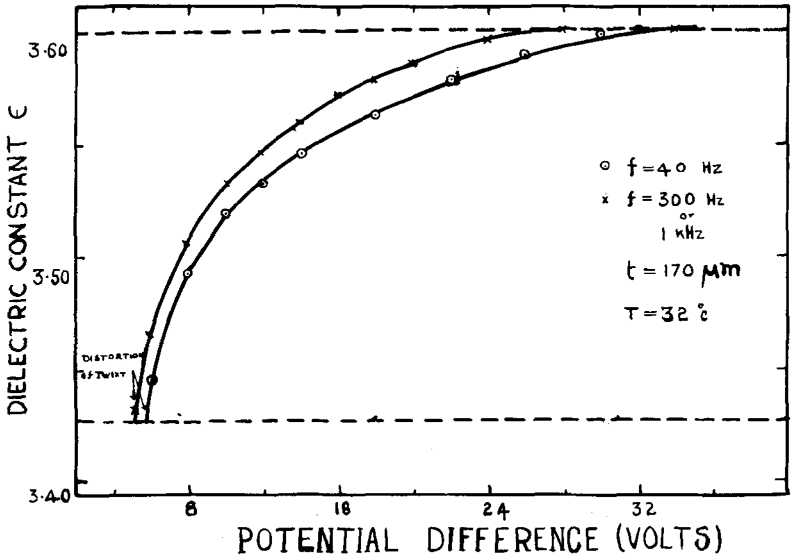


FIGURE 3 Dielectric constant ϵ of twisted nematic MBAB at 1 MHz as a function of externally applied potential difference of various frequencies. Temperature = 32 °C, thickness = 170 μm.

CONCLUSIONS

The interesting aspects of the work reported here are 1) the use of high frequency dielectric measurements to probe the molecular alignment of a nematic director possessing positive dielectric anisotropy under the influence of low frequency electric and magnetic fields. 2) the effect of thickness of the sample to respond to the relative effectiveness of E and H fields for an ordering of the molecules such that the average angle of rotation of the nematic director is 45 ° with respect to both the fields. 3) the correlation of optical observations with the changes in dielectric measurements and molecular alignment. 4) the effect of conduction effects and the use of dielectric measurements to probe the twisted nematic to nematic transition.

The present experimental studies are useful to infer the presence of conduction induced alignment in low frequencies, the cut-off frequency which separates the conduction and dielectric regimes and the dielectric regime where the sudden switching of molecular alignment took place. Furthermore the relative effectiveness of electric to magnetic fields (E/H) for the average nematic order parameter i.e., when the molecular directors are 45 ° to both the fields is constant for different thick samples of MBAB and EBAB. The (E/H) values in Tables IIIa and b correspond to the average state of alignment. The decrease in (E/H) value from 0.97 for MBAB to 0.94 for EBAB can be explained as the increase in $\Delta\epsilon$. The appearance of domains at the threshold voltages for every frequency coincides with the change in dielectric constant and also to a change in the state of molecular alignment.

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